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# A general strategy for synthesis of metal oxide nanoparticles attached on carbon nanomaterials

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## Abstract

We report a general strategy for synthesis of a large variety of metal oxide nanoparticles on different carbon nanomaterials (CNMs), including single-walled carbon nanotubes, multi-walled carbon nanotubes, and a few-layer graphene. The approach was based on the  $\pi$ - $\pi$  interaction between CNMs and modified aromatic organic ligands, which acted as bridges connecting metal ions and CNMs. Our methods can be applicable for a large variety of metal ions, thus offering a great potential application.

## Introduction

The attachment of nanoparticles (NPs) on carbon nanomaterials (CNMs), including single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), and graphene has attracted great interest, for the nanocomposites not only combine the extraordinary properties of the NPs and CNMs, but also exhibit some new properties caused by the interaction between them [1,2]. For examples, when the light-harvesting NPs, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{CdSe}$ , were attached on carbon nanotubes (CNTs) with high conductivity, the photocatalytic properties increased dramatically [3-5]. In addition, CNTs with large surface areas are ideal supporting materials for catalysts NPs, leading to improvements in the efficiency of the catalysts [6-8]. A lot of approaches including assembling pre-synthesized NPs as building blocks on CNTs, and spontaneous formation of NPs on CNTs, have been applied to prepare NPs/CNTs [9-14]. The previous reports mainly focused on attaching NPs on MWNTs by using benzyl alcohol or pyrene derivatives as linkages [15,16]. Development to SWNTs and graphene, both with well-defined structures, may provide important information to explore the mechanisms of the enhanced properties of NPs after attached on CNMs. However, it still remains a challenge to fabricate uniform NPs/CNMs nanocomposites in a controlled manner. Here we present a unified strategy for synthesis of a large variety of NPs of metal oxides, including

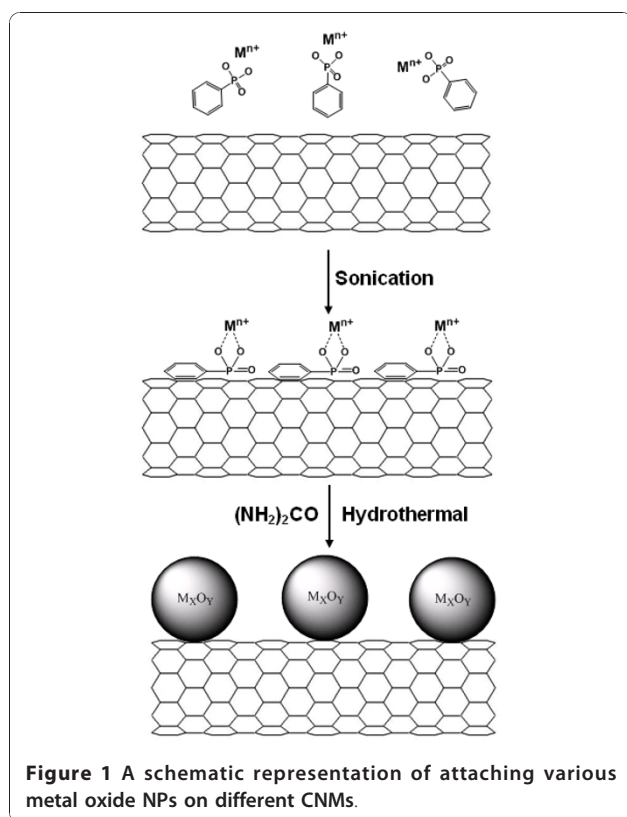
transition and rare earth metal oxides on SWNTs, MWNTs, and a few-layer graphene. The strategy was based on a noncovalent  $\pi$ - $\pi$  interaction between delocalized  $\pi$ -electrons of CNMs and aromatic organic compounds, in this case phenylphosphonic acid, which acid tail can be connected with metal ions. After a hydrothermal treatment, the metal oxides NPs were formed and strongly anchored to the surface of CNMs.

## Experimental sections

In our experiments, MWNTs (purity 95%, 20-30 nm in diameters) were obtained from Shenzhen Nanotech Port (Shenzhen, China) and used as received, SWNTs (purity 99%, 1.4 nm in diameter) were produced by our recent methods [17], and graphene was produced by a modified arc-discharged [18]. The experimental scheme is shown in Figure 1: metal ions were ligated by phenylphosphonic acid, which was then connected with CNMs via noncovalent  $\pi$ - $\pi$  interaction after sonication, then  $(\text{NH}_2)_2\text{CO}$  was added. The solution was transferred to an autoclave and incubated by a hydrothermal treatment. The hydrothermal reaction of metal ions and urea will result in the formation of metal oxide NPs [19]. The final precipitates were filtered and washed several times with water. The samples were characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). See Additional file 1 (SI 1) for more experimental details. In this study, phenylphosphonic acid played a key role on attaching NPs on CNMs. For comparison, a TEM image of the typical products without phenylphosphonic acid was shown in Additional file 1 (SI 2). The particles size

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was obviously larger and did not connect with SWNTs. We also checked the intermediate product after sonication by TGA. The TGA measured the total metal content with a heating rate of 10°C/min in air. The results proved that there was weak interaction between metal ions and CNMs without phenylphosphonic acid. The TGA residue (mainly iron oxide) of the products, made from SWNTs sonicated with only  $\text{Fe}^{3+}$ , was nearly zero. The results proved that without phenylphosphonic acid, the interaction between  $\text{Fe}^{3+}$  and SWNTs was so weak that the metal ions were easily washed away. On the contrary, the resulting residue from SWNTs sonicated with  $\text{Fe}^{3+}$  was around 20%. The results provided direct evidence that phenylphosphonic acid acted as bridges connecting metal ions and CNMs.

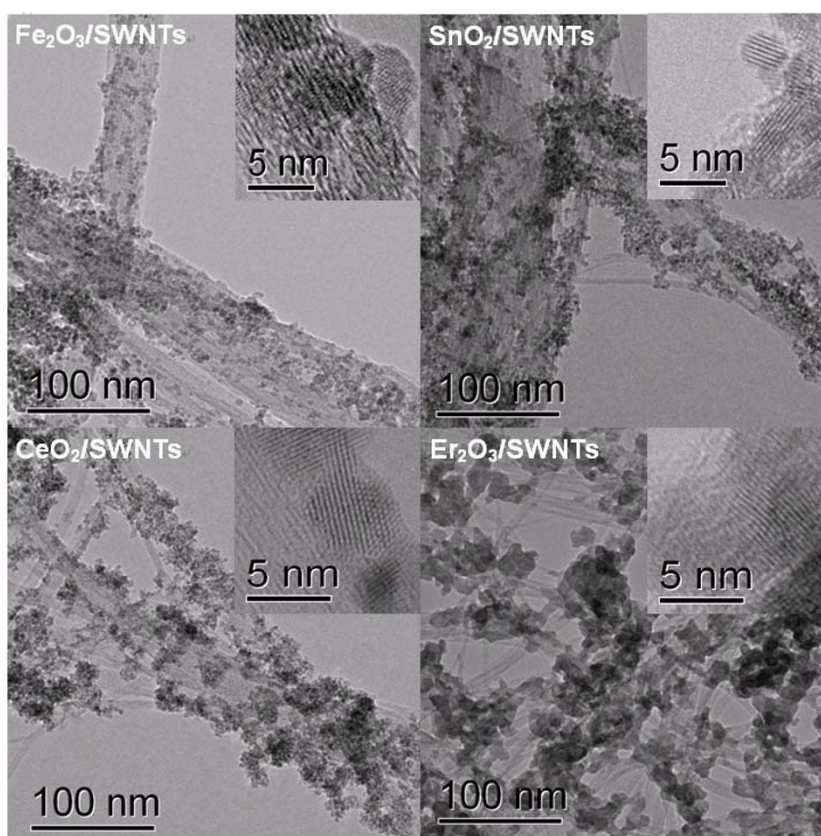
## Results and discussion

Figure 2 shows TEM images of typical samples of  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ , and  $\text{Er}_2\text{O}_3$  on SWNTs, respectively. The SWNTs without NPs attachment were seldom observed by TEM observation. The sizes and loading ratio of NPs on SWNTs can be controlled by altering temperature, the ligand, and the initial concentrations of the metal ions. It is worth to note that the loading ratio in Figure 2 was relatively high, around 80%, resulting in the agglomerating of the NPs on the CNMs. The interface

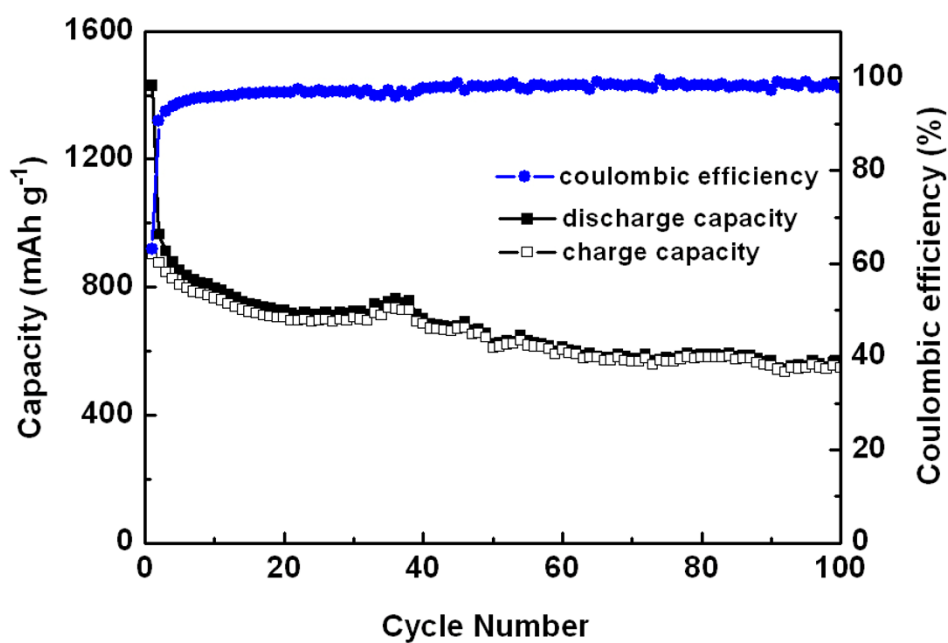
between NPs and CNMs is not prominent. When we decreased the loading ratio, the uniformly dispersed NPs were appeared on the surface of CNMs. See Additional file 1 (SI 3) for the  $\text{SnO}_2$  on SWNTs as example. Inserted images corresponding to their high resolution (HR) TEM images indicated that the metal oxide NPs were usually in round shapes binding on SWNTs. HR-TEM images revealed the detailed structures of these nanocrystals. Typical HR-TEM image of  $\text{Fe}_2\text{O}_3$  nanocrystals with diameters of approximately 4 nm presents a crystal lattice of approximately 0.25 nm, corresponding to (110) planes of  $\alpha\text{-Fe}_2\text{O}_3$ . The result was accorded with XRD pattern shown in Additional file 1 (SI 3). The regular interplanar spacing of 0.33 nm for  $\text{SnO}_2$ , (200) planes of  $\text{CeO}_2$ , respectively. However, as for the rare earth metal oxide  $\text{Er}_2\text{O}_3$ , it did not form fine crystalline structures in such reaction conditions. The result was confirmed by the powder XRD pattern shown in Additional file 1 (SI 3). One might expect formation of crystalline  $\text{Er}_2\text{O}_3$  NPs after thermal annealing. The nanohybrid materials have many potential applications compared with the isolated NPs, because SWNTs act as carrier to stabilize NPs, maintaining their integrity. We selected  $\text{Fe}_2\text{O}_3$ /SWNTs as a model case for superior anode materials of lithium ion batteries.

Figure 3 displays the high reversibility of the electrochemical reactions of  $\text{Fe}_2\text{O}_3$ /SWNTs nanohybrid over many charge-discharge cycles and the columbic efficiency. After 100 cycles at 150  $\text{mA g}^{-1}$ , it still remained a high reversible capacity of 560  $\text{mAh g}^{-1}$ , which was significantly higher than that of graphite (372  $\text{mAh g}^{-1}$ ) and  $\text{Fe}_2\text{O}_3$  nanotube (510  $\text{mAh g}^{-1}$  at 100  $\text{mA g}^{-1}$ ) [20]. The columbic efficiency of the whole 100 cycles was around 97%. Our previous results indicated that the SWNTs produced by our method provided low Li insertion/de-insertion capabilities, around 200  $\text{mAh g}^{-1}$  [21], so the superior capabilities of  $\text{Fe}_2\text{O}_3$  NP/SWNTs electrode were ascribed to the reactions involving  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  conversions. The performance of the nanocomposites was mainly determined by the particle sizes and loading ratio of the NPs.

Our method was based on  $\pi$ - $\pi$  interaction between ligand and CNMs, thus can also be generally applicable to graphene and MWNTs. Shown in Figure 4 are TEM images of  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ , and  $\text{TiO}_2$  NPs assembled with a few-layer graphene. The diameters and loading ratio of NPs were controlled by temperature and the mole ratio of metal ions to graphene nanosheets. Typically, the particles are remarkably smaller when deposited on CNMs compared with unanchored phase, since CNMs can prevent crystal growth during crystallization. We also succeeded in introducing NPs of different rare

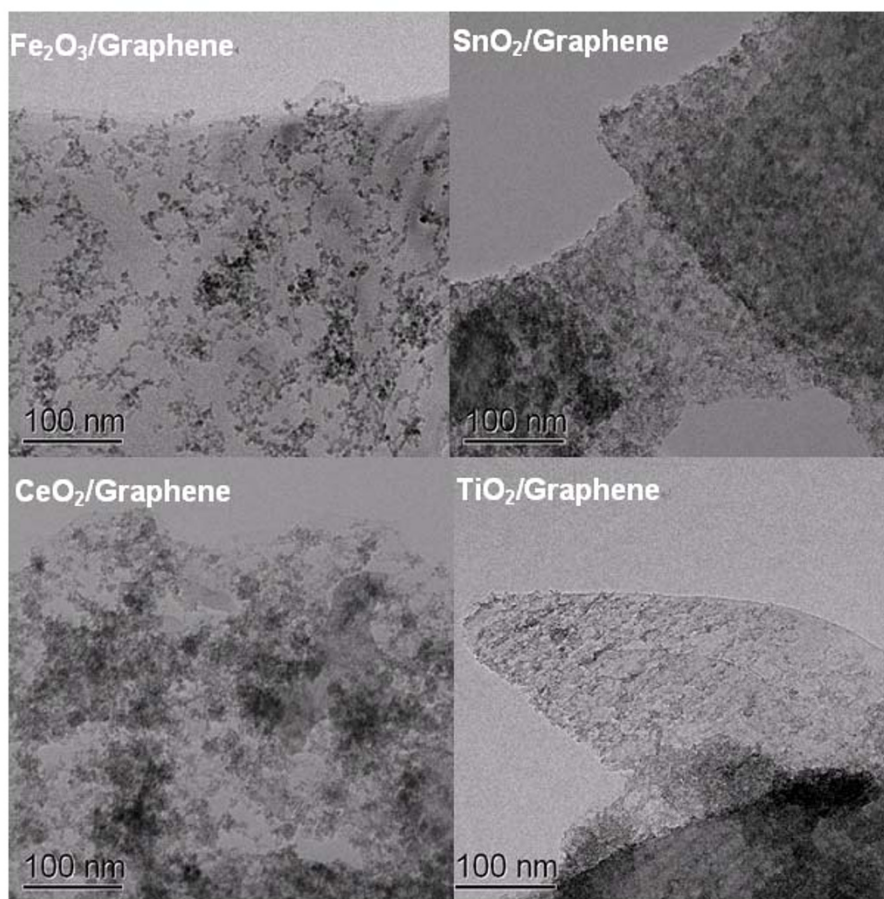


**Figure 2** TEM images of various metal oxide NPs of  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ , and  $\text{Er}_2\text{O}_3$  on SWNTs.



**Figure 3** Cycle performance and coulombic efficiency of  $\text{Fe}_2\text{O}_3/\text{SWNTs}$  nanohybrids with a current density of  $150 \text{ mA g}^{-1}$ .





**Figure 4** TEM images of various metal oxide NPs of Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, CeO<sub>2</sub>, and TiO<sub>2</sub> on a few-layer graphene.

earth metal oxides on MWNTs. See Additional file 1 (SI 5) for more details.

## Conclusion

In summary, we report a general strategy for synthesis of a large variety of metal oxide NPs on CNMs, including SWNTs, MWNTs, and a few-layer graphene. The approach was based on the  $\pi$ - $\pi$  interaction between CNMs and modified aromatic organic ligands, which acted as bridges connecting metal ions and CNMs. Our methods can be applicable for a large variety of metal ions. By adopting bi-metal or even tri-metal precursors in a certain mole ratio, composite oxide nanocrystals with novel structures and multi-function deposited on different CNMs can be effectively prepared through this method. The new class of hybrid nanomaterials offers a great potential application in sustainable energy, environment, and even biomedicine.

## Additional material

**Additional file 1: Supporting information.** Experimental details, the proof of  $\pi$ - $\pi$  interaction between ligand and CNMs, the linkage of NPs and CNMs, electrochemical measurements and NPs on MWNTs.

## Abbreviations

CNMs: carbon nanomaterials; CNTs: carbon nanotubes; MWNTs: multi-walled carbon nanotubes; NPs: nanoparticles; SWNTs: single-walled carbon nanotubes; TEM: transmission electron microscope; TGA: thermogravimetric analysis; XRD: X-ray diffraction.

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## Authors' contributions

YZ carried out experiments, analysed and discussed data and wrote the paper; JL carried out experiments; CW carried out experiments, LG

conceived, designed and carried out experiments, analysed and discussed data and wrote the paper.

#### Competing interests

The authors declare that they have no competing interests.

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